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(71) Applicant: **GENERAL ELECTRIC COMPANY**
1 River Road
Schenectady, N.Y. 12151(US)

(72) Inventor: **Avakian, Roger W.**
General Electric Plastics B.V., P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)
Inventor: **Claesen, Christianus Adrianus Arnoldus**
General Electric Plastics B.V., P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)
Inventor: **Kite, Neil Tony Geoffrey**
General Electric Plastics B.V., P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)
Inventor: **Viersen, Frits Jan**
General Electric Plastics B.V., P.O. Box 117
NL-4600 AC Bergen op Zoom(NL)

(74) Representative: **Schüler, Horst, Dr. et al**
General Electric Praunheimer Landstrasse 50
D-6000 Frankfurt 90(DE)

(54) Method of preparing beads of polyphenylene ether-polystyrene, beads thus formed.

(57) In the preparation of fine beads consisting of a polyphenylene ether - polystyrene mixture, a capped polyphenylene ether is preferably used. It has been found possible to cap the polyphenylene ether in the presence of the styrene monomer.
This provides practical advantages.

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Method of preparing beads of polyphenylene eth r-polystyrene, beads thus formed

The invention relates to a method of preparing beads built up substantially from a polymer mixture of a polyphenylene ether and a polyvinylaromatic compound, in which a polyphenylene ether is mixed with a vinylaromatic monomer and is suspended in an aqueous medium; a suspension polymerisation catalyst is added; the vinylaromatic monomer is polymerised and the suspended particles are separated from the resulting suspension.

The invention also relates to a method of preparing expandible fine beads in which during or after the preparation according to the above-mentioned method an easily volatilisable hydrocarbon or halogenated hydrocarbon is incorporated in the particles.

The invention also relates to the beads obtained according to either of the two mentioned methods.

EP-A-294783 discloses a method of preparing expandible thermoplastic beads consisting substantially of a polyphenylene ether and a vinylaromatic polymer. In the known method a polyphenylene ether together with a vinylaromatic monomer is suspended in an aqueous medium. According to this prior art so-called capped polyphenylene ethers may be used as a polyphenylene ether. Such capped polyphenylene ethers and methods of preparing the same are generally known. For this purpose reference may be made, for example, to US-A-3,375,228, US-A-4,048,143 and US-A-4,760,118. The use of capped polyphenylene ethers has been found to present advantages in the suspension polymerisation of vinylaromatic monomers. It had already been found in the bulk polymerisation of vinylaromatic monomers in the presence of a polyphenylene ether that the use of capped polyphenylene ethers presents advantages (see US-A-4,148,843). However, the use of capped polyphenylene ethers requires an extra reaction step after the preparation of the polyphenylene ether.

It has been found that the capping of the polyphenylene ether, resulting in a decrease of the content of terminal hydroxyl groups, may also be carried out in the presence of the vinylaromatic monomer before the suspension polymerisation catalyst is added. This means that an extra preparation step in a separate reactor can be avoided.

The method according to the invention is characterised in that the content of terminal hydroxyl groups of the polyphenylene ether before suspending in the aqueous medium in the presence of the vinylaromatic monomer is decreased by the addition of a capping agent.

The polyphenylene ether may be capped while forming, for example, an O-C, O-P or O-Si bond from the phenolic hydroxyl groups which usually are present in the polyphenylene ether. O-C ester bonds can be obtained by reaction of the phenolic hydroxyl groups with acid chlorides or acid anhydride in the presence of a base. O-C ether bonds can be obtained, for example, by reaction with dimethyl sulphate in the presence of a base. O-P bonds can be obtained by reaction with, for example, $POCl_3$. O-Si bonds can be obtained by reaction with silylating agents, for example, bis(trimethylsilyl) sulphate, trimethyl chlorosilane, and trimethyl silylcyanide. The above-mentioned reactions are known per se.

The capping reaction is preferably carried out by the addition of an acid anhydride or acid chloride in combination with an organic base.

A secondary or tertiary amine, for example, a trialkylamine, pyridine, N,N-dialkylamine pyridine is preferably used as an organic base.

In the method according to the invention a polyphenylene ether is used. Polyphenylene ethers are generally known polymers. Suitable polyphenylene ethers are described, for example, in the above-mentioned EP-A-294,783 and the literature references mentioned therein. Polyphenylene ethers usually have terminal hydroxyl groups, sometimes referred to as phenolic terminal groups. Polyphenylene ethers having such terminal groups are used as a starting material in the method according to the invention.

In the method according to the invention a suspension is prepared of the polyphenylene ether and a vinylaromatic monomer. The weight ratio of the polyphenylene ether and the vinylaromatic monomer in the suspension may be chosen between 5-80 and 95-20; said ratio preferably is between 10-60 and 90-40. Examples of suitable vinylaromatic monomers are styrene, alpha-methyl styrene, ethyl styrene, halogenated styrene compounds, vinyltoluene, and mixtures of one or more of these compounds. It is also possible to use a mixture consisting of at least 50% of a vinylaromatic monomer and a monomer which can be copolymerised therewith, for example, acrylonitrile, methylmethacrylate or methylacrylate.

Th suspension in aqueous medium can be prepared in various manners, for example, by dissolving a polyphenylene ether in the form of a powder or of particles having a diameter of approximately 0.05-5 mm in the vinylaromatic monomer and suspending the resulting solution in water. In this method a dispersing agent, for example, polyvinyl alcolhol, m thyl cellulose, and the like, is used. Other possibilities to obtain a suspension are described in EP-A-294783. In th m thod according to the invention a capping agent is

added to the polyphenylene eth r, after mixing same with th vinylaromatic monomer, to decr ase the content of terminal hydroxyl groups of the polyphenylene ether. This content is preferably reduced to a content of less than 20% of the originally present content.

An acid chloride or an acid anhydride may be added as a capping agent. Suitable capping agents are, for example, acetyl chloride, benzoyl chloride, acetic acid anhydride, (meth)acryloyl chloride. The capping agents are preferably used in combination with an organic base, for example, triethylamine, pyridine, N,N-dimethylamino pyridine.

After the capping reaction the resulting product is processed to beads by means of suspension polymerisation in the manner as described in EP-A-294,783. During or after the polymerisation reaction an easily volatilisable hydrocarbon or halogenated hydrocarbon may be incorporated in the said beads.

The invention will now be described in greater detail with reference to the ensuing specific examples.

Examples

Solutions of 100 g of poly(2,6-dimethyl-1,4-phenylene ether) in 400 g of styrene monomers were prepared. The polyphenylene ether used had an intrinsic viscosity of approximately 0.57 dl per gram measured in a chloroform solution at 25° C. The content of terminal hydroxyl groups was 1735 ppm.

In order to readily dissolve the polyphenylene ether, heating was carried out up to approximately 110° C. At that temperature various capping agents and amines, as indicated in the table herein-after, were added. 300 g of the solution thus obtained were then suspended in 600 ml of water by means of 3 g of polyvinyl alcohol. The polymerisation reaction was carried out by adding 0.75 g of azobis isobutyronitrile. In all the cases a substantially complete polymerisation of the styrene was obtained.

TABLE

Example	Capping agents (quantity in grammes)	OH content after capping (ppm)	Duration of the capping reaction (min.)	Bead dimension (d in mm)
1	AcCl(6.5) + dmap(10.2)	105	15	0.1-1.1
2	ditto	less than 50	60	0.2-0.6
3	AcCl(6.5) + tea(8.5)	55	15	0.2-4*
4	ditto	25	30	0.2-7*
5	ditto	30	60	0.1-5*
6	AcCl(6.5).pyr(6.6)	90	15	0.2-0.6
7	ditto	not determined	30	0.2-1.0
8	Ac_2O(8.5) + dmap(1)	85	15	0.1-0.6
9	ditto	70	30	0.2-0.5
10	ditto	30	60	0.1-0.5
11	BzCl(11.7) + dmap(10.2)	130	15	0.2-1.0
12	ditto	not determined	30	0.2-0.8

AcCl = acetyl chloride
AC_2O = acetic acid anhydride
BzCl = benzoyl chloride
dmap = N,N-dimethylamine pyridine
tea = triethyl amine
pyr = pyridine

* non-spherical particles; the largest dimension is indicated

Claims

1. A method of preparing beads built up substantially from a polymer mixtur of a polyphenylene eth r

and a polyvinylaromatic compound, in which a polyphenylen ether is mixed with a vinylaromatic monom r and is suspended in an aqueous medium; a suspension polymerisation catalyst is added; the vinylaromatic monomer is polymerised and the suspended particles are separated from the resulting suspension, characterised in that the content of terminal hydroxyl groups of the polyphenylene ether, before suspending in the aqueous medium in the presence of the vinylaromatic monomer is decreased by the addition of a capping agent.

2. A method as claimed in Claim 1, characterised in that the content of terminal hydroxyl groups of the polyphenylene ether is decreased by the addition of an acid anhydride or acid chloride in the presence of an organic amine compound.

3. A method as claimed in Claim 2, characterised in that N,N-dimethylamino pyridine, pyridine or triethylamine is used as an organic base.

4. A method as claimed in Claim 1, characterised in that the content of terminal hydroxyl groups is decreased to less than 20 % of the originally present content.

5. A method of preparing expandible beads in which during or after the preparation of the method as claimed in Claim 1 an easily volatilisable hydrocarbon or halogenated hydrocarbon is incorporated in the particles.

6. Shaped beads obtained by using the method as claimed in Claim 1.

7. Shaped beads obtained by using the method as claimed in Claim 5.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 0401

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-3 384 682 (ERCHAK et al.) * Claims *	1-7	C 08 F 283/08 C 08 G 65/48 C 08 J 9/18 C 08 J 9/20 // (C 08 F 283/08 C 08 F 212:04)
Y	EP-A-0 261 574 (GENERAL ELECTRIC CO.) * Claims; example 24; procedure A,B,C,D *	1-7	
D,A	US-A-4 148 843 (GOSSENS) * Claims *	1-7	
D,A	EP-A-0 294 783 (GENERAL ELECTRIC CO.)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 08 G
C 08 F
C 08 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29-03-1990	LOISELET-TAISNE S.M.T.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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